

Optimization of process parameters for ruthenium nanoparticles synthesis by (w/o) reverse microemulsion

S. U. Nandanwar · J. Barad · S. Nandwani ·
M. Chakraborty

Received: 24 February 2014 / Accepted: 8 May 2014 / Published online: 1 June 2014
© The Author(s) 2014. This article is published with open access at Springerlink.com

Abstract Taguchi OA factorial design method was used to identify the several factors that might affect the particle size of ruthenium nanoparticles prepared by the mixing of two reactive microemulsions. In the present work, the objective of evaluating the factors influencing the particle size had been improvised by studying two qualitative factors viz., effect of different reducing agents and effect of different co-surfactants. Using orthogonal experimental design and analysis technique, the system performance could be analyzed with more objective conclusion through only a small number of simulation experiments. Analysis of variance was carried out to identify the significant factors affecting the response and the best possible factor level combination was determined through. It was found that the formation of ruthenium nanoparticles, microemulsions were greatly influenced by the type of reducing agent used in the technique followed by water-to-surfactant molar ratio.

Keywords Taguchi method · ANOVA · Ru nanoparticles · Microemulsions technique

Introduction

Nowadays, there is a great interest in transition metal nanotechnologies and the development of simple and reproducible methods to synthesize the nanoparticles by the various research groups as they have shown maximum

application in magnetism, semiconductor, optoelectronics, and especially in the field of catalysis (Kim et al. 2007). Ruthenium, transition metal has shown very unique and interesting catalytic activities for many reactions (Lu et al. 2008). Owing to huge application in field of catalysis many research groups were focused to synthesize the Ru nanoparticles. Generally, various methods were available for synthesis of Ru nanoparticles, such as refluxing a polyol solution (Yan et al. 2001), thermal decomposition of $\text{Ru}_3(\text{CO})_{12}$ (Motoyama et al. 2006), sonochemical reduction (He et al. 2006), microwave-assisted reduction (Zhang et al. 2007a, b; Zawadzki and Okal 2008), organometallic synthesis (Debouttiere et al. 2009), solvothermal (Nandanwar et al. 2011a, b), chemical reduction method (Patharkar et al. 2013), and also by microemulsion technique (Kim et al. 2007; Xiong and Manthiram 2005; Rojas et al. 2005; Zhang et al. 2007a, b; Nandanwar et al. 2011a, b).

Kim et al. (2007), synthesized the bimetallic, platinum–ruthenium transition metal nanoparticles by chemical reduction using sodium borohydride in reverse microemulsion of water/isooctane/Igepal CA-630/2 propanol for fuel cell catalyst. Pt–Ru/C catalysts were synthesized using a reverse microemulsion using sodium *bis*(2-ethylhexyl) sulfosuccinate (AOT) as the surfactant and heptane as the oil phase (Xiong and Manthiram 2005). Carbon supported Pt and Pt–Ru electrocatalyst was prepared by the microemulsion technique (Rojas et al. 2005). Zhang et al. (2007a, b), prepared the ternary platinum–ruthenium–nickel nanoparticles by w/o reverse microemulsion. The composition and size of ternary Pt–Ru–Ni nanoparticles were controlled by adjusting the initial metal salt solution and preparation conditions. Recently, Nandanwar et al. (2011a, b), synthesized ruthenium nanoparticles using two reactants ruthenium chloride and sodium borohydride by microemulsion method.

S. U. Nandanwar · J. Barad · S. Nandwani ·
M. Chakraborty (✉)
Department of Chemical Engineering, S. V. National Institute of
Technology, Surat 395 007, Gujarat, India
e-mail: mch@ched.svnit.ac.in

The microemulsion is one of the best techniques to synthesize ruthenium nanoparticles at ambient condition with narrow size distribution. Microemulsions are amphiphile stabilized transparent, optically isotropic and thermodynamically stable dispersions of water, oil and surfactant. Water-in-oil (w/o) microemulsion is one of the most recognized methods due to its several advantages, such as demanding no extreme pressure or temperature control, easy to handle, soft chemistry, and requiring no special or expensive equipment (Charinpanitkul et al. 2005). This technique has already 25 years of history, but the mechanisms to control the final size and the size distribution are still not known.

In the present article, highly monodisperse ruthenium nanoparticles were synthesized by w/o microemulsion system at room temperature. The various parameters that influenced on the size of particles like surfactant concentration, water-to-surfactant molar ratio (ω), concentration of the precursor, reducing agent-to-ruthenium trichloride molar ratio (R), effect of cosurfactant and effect of different reducing agent etc. were studied. Taguchi OA fractional factorial design method is used to optimize all the six parameters to synthesize the smallest ruthenium nanoparticles.

Taguchi OA fractional factorial design

The experimental work had been designed in a sequence of steps to insure that data are obtained in a way that its analysis will lead immediately to valid statistical inferences. This research methodology is termed as design of experiment (DOE) methodology. DOE using Taguchi approach attempts to extract maximum important information with minimum number of experiments (Lazic 2004). Taguchi techniques are experimental design optimization techniques that use standard orthogonal arrays (OA) for forming a matrix of experiments. An orthogonal array is a fractional factorial experimental matrix that is orthogonal and balanced. The ASQC (1983) Glossary & Tables for Statistical Quality Control defines fractional factorial design in the following way: a factorial

experiment is one in which only an adequately chosen fraction of the treatment combinations required for the complete factorial experiment is selected to be run.

In the present work, six parameters each at three levels are selected to evaluate the size of ruthenium nanoparticles obtained after mixing two microemulsions during each run. The factors to be studied are mentioned in Table 1. Based on Taguchi orthogonal array factorial designs method, the L_{27} -OA is constructed. A L_{27} -OA is chosen to evaluate some of the two-way interactions.

Experimental data

Materials

Transition metal, ruthenium trichloride ($\text{RuCl}_3 \cdot n\text{H}_2\text{O}$, Ru Content $\geq 37\%$), cyclohexane, *n*-butanol, hydrazine hydrate (80 %) and methanol all were of analytical grades and purchased from Finar chemicals, India. The hydroxylammonium sulphate and *n*-pentanol were purchased from National chemicals, India. Sodium borohydride (NaBH_4 , 95 %) and non-ionic surfactant, polyoxyethylene octyl phenyl ether (Triton X-100) were purchased from S. D. fine chemicals, India. All the chemicals were used without further purification. Distilled water was used throughout the experiments for preparing all the aqueous solutions.

Synthesis of ruthenium nanoparticle

Synthesis of monodisperse ruthenium nanoparticles by reverse microemulsion was reported in our previous paper (Nandanwar et al. 2011a, b). To prepare (0.2 mol/L) concentration of surfactant (Triton X-100), known amount of Triton X-100 was dissolved into cyclohexane and vigorously stirring by high-speed blender. The concentration of surfactant was varied by increasing amount of Triton X-100 in cyclohexane. RuCl_3 -aqueous/cyclohexane/Triton X-100 microemulsion was prepared by drop wise addition of RuCl_3 aqueous solution (0.1 M) into the prepared mixture of cyclohexane-Triton X-100. The known quantity of

Table 1 Factors and their levels in the experimental design

Level	Water-to-surfactant molar ratio	Effect of surfactant concentration	Effect of RuCl_3 concentration	Effect of molar ratio of reducing agent	Effect of co-surfactant	Different reducing agent
1	3	0.2	0.1	3	No co-surfactant	NaBH_4
2	5	0.3	0.2	5	Pentanol	Hydrazine
3	7	0.4	0.3	10	Butanol	Hydroxylammonium

Table 2 L_{27} -OA and response values

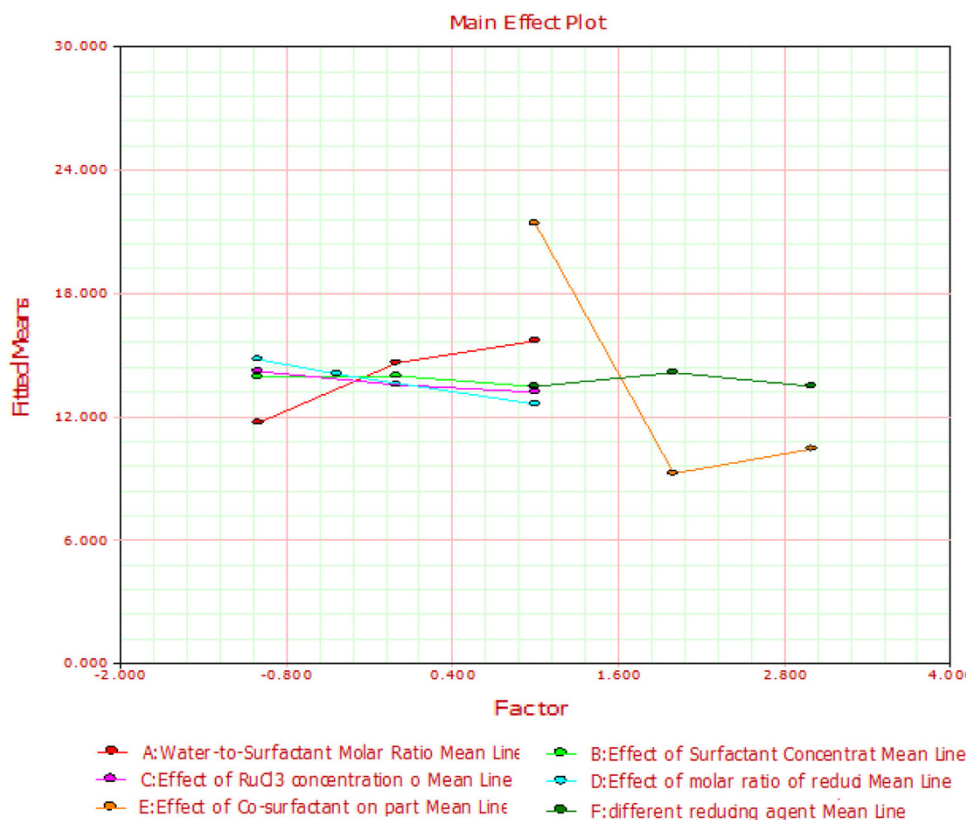
Run no.	Water-to-surfactant molar ratio	Effect of surfactant concentration	Effect of RuCl_3 concentration	Effect of molar ratio of reducing agent	Effect of co-surfactant	Different reducing agent	(Number %) particle size (nm)
1	3	0.2	0.1	3	No co-surfactant	NaBH_4	19.01
2	3	0.2	0.1	3	<i>n</i> -Pentanol	Hydrazine	8.29
3	3	0.2	0.1	3	<i>n</i> -Butanol	Hydroxylammonium	9.47
4	3	0.3	0.2	5	No surfactant	NaBH_4	17.21
5	3	0.3	0.2	5	<i>n</i> -Pentanol	Hydrazine	8.01
6	3	0.3	0.2	5	<i>n</i> -Butanol	Hydroxylammonium	9.35
7	3	0.4	0.3	10	No co-surfactant	Hydrazine	15.07
8	3	0.4	0.3	10	<i>n</i> -Pentanol	NaBH_4	7.83
9	3	0.4	0.3	10	<i>n</i> -Butanol	Hydroxylammonium	9.08
10	5	0.2	0.2	10	No co-surfactant	Hydrazine	22.07
11	5	0.2	0.2	10	<i>n</i> -Pentanol	Hydroxylammonium	8.34
12	5	0.2	0.2	10	<i>n</i> -Butanol	NaBH_4	10.17
13	5	0.3	0.3	3	No co-surfactant	Hydrazine	23.09
14	5	0.3	0.3	3	<i>n</i> -Pentanol	Hydroxylammonium	10.74
15	5	0.3	0.3	3	<i>n</i> -Butanol	NaBH_4	11.52
16	5	0.4	0.1	5	No co-surfactant	hydrazine	23.12
17	5	0.4	0.1	5	<i>n</i> -Pentanol	Hydroxylammonium	10.75
18	5	0.4	0.1	5	<i>n</i> -Butanol	NaBH_4	11.72
19	7	0.2	0.3	5	No co-surfactant	Hydroxylammonium	24.91
20	7	0.2	0.3	5	<i>n</i> -Pentanol	NaBH_4	10.23
21	7	0.2	0.3	5	<i>n</i> -Butanol	Hydrazine	11.27
22	7	0.3	0.1	10	No co-surfactant	Hydroxylammonium	24.39
23	7	0.3	0.1	10	<i>n</i> -Pentanol	NaBH_4	10.19
24	7	0.3	0.1	10	<i>n</i> -Butanol	Hydrazine	11.37
25	7	0.4	0.2	3	No co-surfactant	Hydroxylammonium	25.07
26	7	0.4	0.2	3	<i>n</i> -Pentanol	NaBH_4	10.31
27	7	0.4	0.2	3	<i>n</i> -Butanol	Hydrazine	11.48

aqueous solution was added into Triton X-100 in cyclohexane mixture, to get desired water-to-surfactant molar ratio (ω) of 5. Uniform stirring was maintained with ultraturax T25 high-speed mechanical stirrer (Ultraturax® IKA WERKE, GmbH & Co. KG) at 6,500 rpm for 5 min at room temperature for proper mixing. Secondly, NaBH_4 -aqueous/cyclohexane/Triton X-100 microemulsions with same ω value was prepared by using aqueous solution of NaBH_4 (0.5 M). Two microemulsions were mixed directly under adequate stirring for 15 min at room temperature. The mixture was destabilized by methanol. Finally, metal

nanoparticles were separated by high-speed centrifugation to accumulate concentrated Ru colloidal nanoparticles for further characterization.

Design of experiments

The experiments were carried out according to the L_{27} -OA. The size of ruthenium nanoparticles represented as (number %) particle size (nm) was considered as Taguchi array response. After an experimental design is created, the

Fig. 1 Main effect plot

combinations of factor levels are randomly run and the data is grouped with the corresponding experimental run. The L_{27} -OA and response values (Number %) in terms of particle size (nm) are shown in Table 2.

Results and discussions

Main effect plot and interaction plot

Main effects plot for the main effect terms viz. factors A, B, C, D, E and F are shown in Fig. 1. However, the main effect plot does not tell, which of the main effect factors are statistically significant (Mendenhall and Sincich 1989). From the main effect plot, it has been observed that the size of ruthenium nanoparticles increases with increasing water-to-surfactant molar ratio (A). Since the interest of the present study lies in achieving smaller ruthenium nanoparticles, a water-to-surfactant molar ratio of 3 is found to be desirable. Because of low water content, the water solubilized in the polar core is bound by the surfactant molecules, which increases the boundary strength and decreases the intermicellar exchange rate among the reverse micelles which controls micellar sizes as well as sizes of the nanoparticles (Nandanwar et al. 2011a, b).

From the plot, it is clear that the size of ruthenium nanoparticles is almost independent of the two factors viz., surfactant concentration (B) and RuCl_3 concentration (C).

It has also been found that the size of ruthenium nanoparticles decreases with an increase in molar ratio of reducing agent (D). At higher molar ratio, higher intramicelles nucleation and growth will be promoted. As reduction takes place at a faster rate so bigger size particles will be generated.

Effect of different types of co-surfactants (E) on the size of ruthenium nanoparticles has also been observed. From the plot, it has been found that ruthenium nanoparticles obtained without co-surfactant is larger than when co-surfactants are used. However, among the two types of co-surfactants used, *n*-pentanol and *n*-butanol, the former gives smaller sized ruthenium nanoparticles. The co-surfactant increases the fluidity of the interface and thus the kinetics of the intermicellar exchange, which in turns ensures a more homogeneous repartition of reactants among droplets (Lopez-Quintela et al. 2004).

Different types of reducing agents (F) also affect the size of the ruthenium nanoparticles. Sodium borohydride is a strong reducing agent in comparison with hydrazine hydrate and hydroxylammonium sulphate. This leads to rate of reduction begin fast and thus rate of nucleation and the particles growth being controlled by the collision,

Fig. 2 Interaction plot for $A \times B$ where (B effect of surfactant concentration)

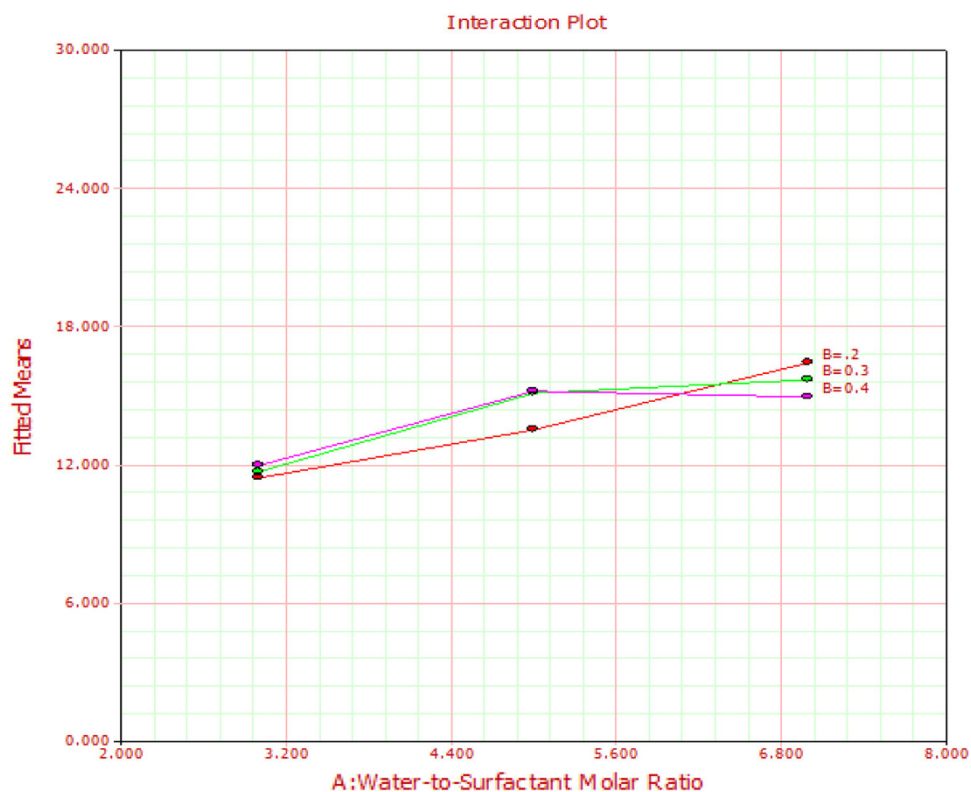


Fig. 3 Interaction plot for $A \times C$ where (C effect of RuCl_3 concentration)

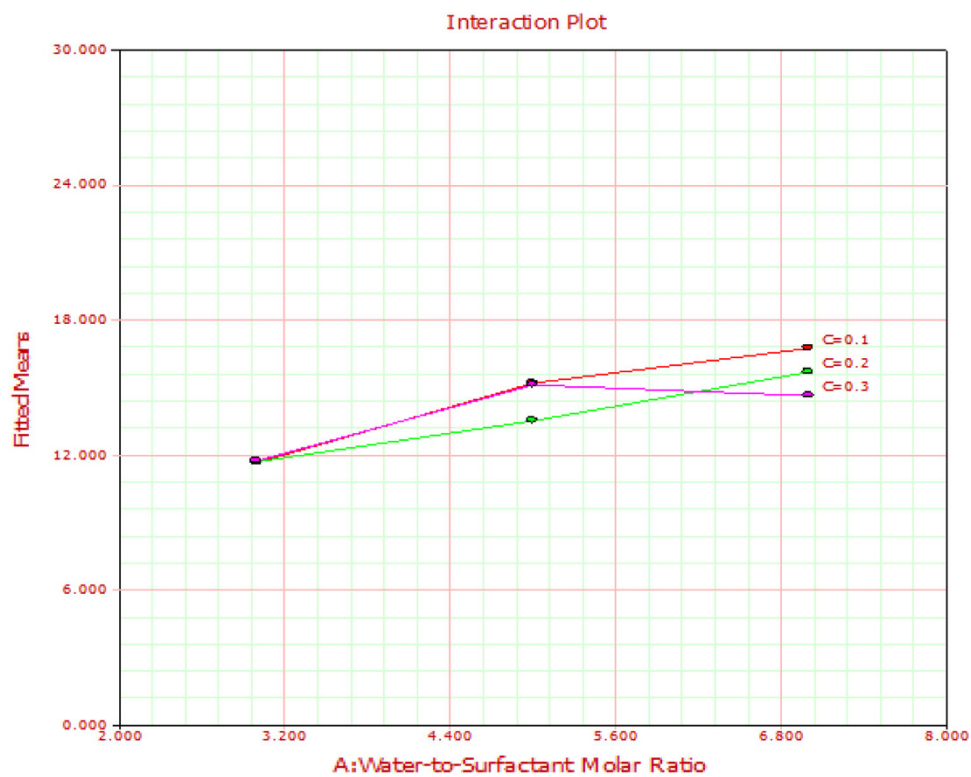
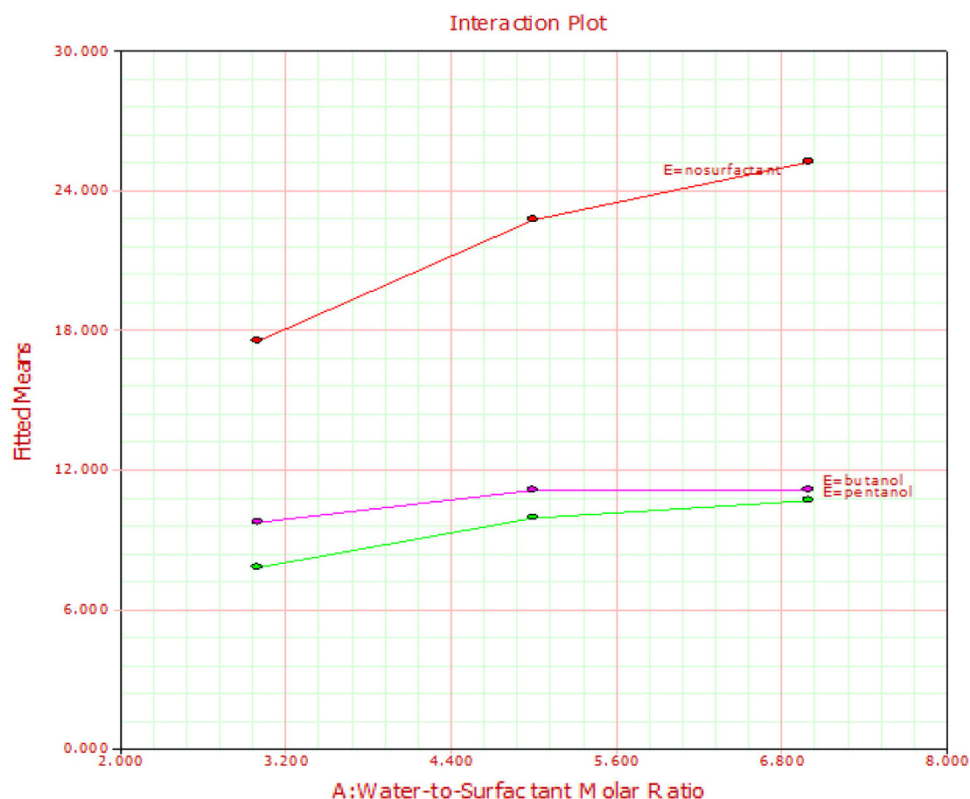


Fig. 4 Interaction plot for $A \times E$ where (E effect of cosurfactant)



fusion and split of the droplets, which results in bigger size but highly monodispersed nanoparticles.

Interaction effects

Interaction means influence of one operating variable on the other operating variable (Mendenhall and Sincich 1989). In the present work three interaction terms have been considered viz., ($A \times B$), ($A \times C$) and ($A \times E$). Whether interactions between factors exist or not can be shown by plotting an interaction plot. Parallel lines in an interaction plot indicate no interaction. However, the interaction plot doesn't tell if the interaction is statistically significant (Clements 1991). Interaction plots are most often used to visualize interactions during DOE. *Reliasoft DOE++1* displays interaction plots for each of the three interaction terms viz., ($A \times B$), ($A \times C$) and ($A \times E$) in Figs. 2, 3 and 4 respectively. Since all the interaction plots have non-parallel lines, interaction exists between all the three interacting factors.

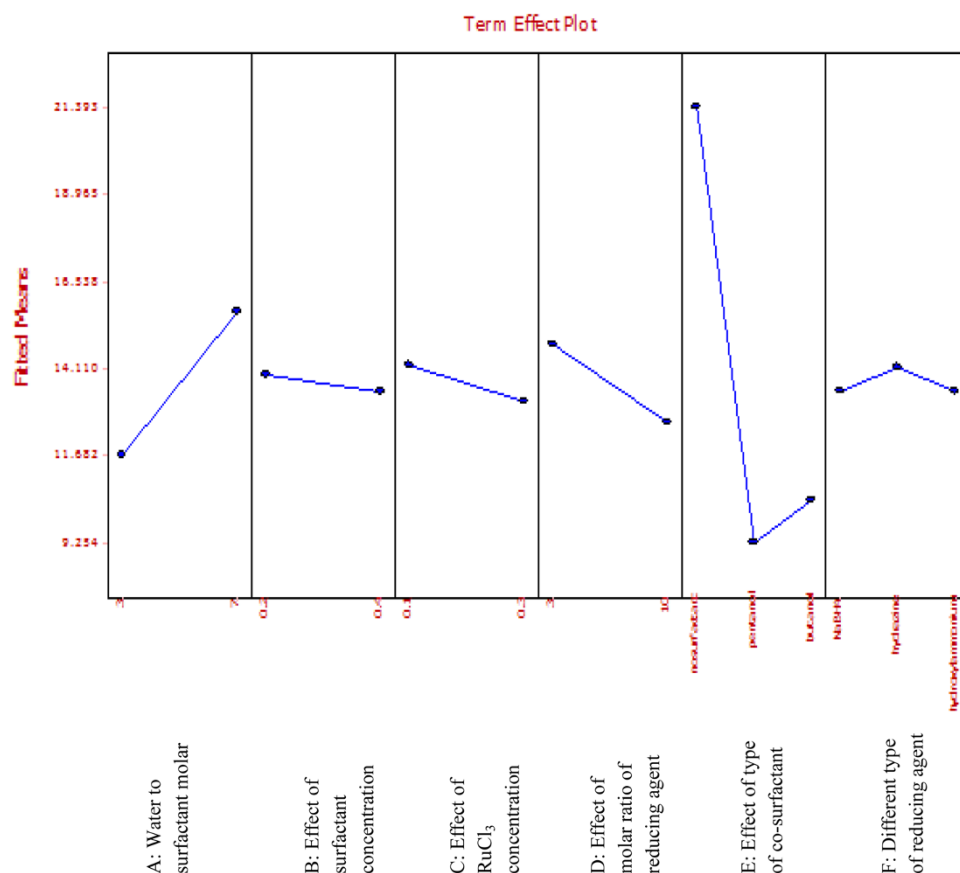
Optimum settings via term effect plot

In the present study, a term effect plot has been used to predict the optimum settings for obtaining smaller ruthenium nanoparticles. The level of each factor that gives smaller sized ruthenium nanoparticles (smaller response 'Y') is

considered. From the term effect plot shown in Fig. 5, it is obvious that a water-to-surfactant molar ratio of '3' gives smaller ruthenium particles. Similarly for the effect of surfactant concentration, effect of RuCl_3 concentration and effect of molar ratio of reducing agent, the levels at which we obtain smallest ruthenium nanoparticles are '0.4', '0.3' and '10' respectively. When using different reducing agents, NaBH_4 gives the smallest nanoparticles and for different types of co-surfactants, *n*-pentanol gives result at optimum level. Thus from the term effect plot, it is observed that the optimum settings for the experimentation of producing ruthenium nanoparticles might be the one shown in Table 3. Using the diagnostic tool from the *Reliasoft* software, it has been observed that the smallest nanoparticles were obtained for the same settings, i.e., a smallest size of '7.83 nm'.

ANOVA table

The analysis of variance (ANOVA) is one of the most commonly used methods of analyzing experiments. In any experiment where several factors are allowed to vary, a situation called experimental error exists. This experimental error creates a background "noise" in the data. ANOVA measures this background noise and also the amount of signal each factor under study creates. If a factor is creating a signal that has more magnitude than the background noise then that factor has a significant effect (3).

Fig. 5 Term effect plot**Table 3** Optimum settings for the experimentation of producing ruthenium nanoparticles

Factors	Optimum level
Water-to surfactant molar ratio	3
Effect of surfactant concentration	0.4
Effect of RuCl ₃ concentration	0.3
Effect of molar ratio of reducing agent	10
Effect of type of co-surfactant	Pentanol
Different type of reducing agent	NaBH ₄

Statistical tests are applied to the data to test for significance or association. The analysis of experiment is done by using *Reliasoft DOE++1* software. The present work has been based on 95 % confidence level ($\alpha = 0.05$) which means that there is a probability of at least 95 % that the result is reliable. In the present study, since orthogonal arrays do not test all variable combinations, the interaction effect of all the parameters could not be taken into optimization process. As a result, necessary two factor interactions, i.e., the combined effect of the factors ($A \times B$), ($A \times C$) and ($A \times E$) where [A Water-to-surfactant molar ratio, B effect of surfactant concentration, C effect of

RuCl₃ concentration and E effect of different co-surfactants] are only considered.

An ANOVA table for the above experiment is given in Table 4. The table reveals the significant effects (in red) and the non-significant effects. It also shows the standard deviation for the statistical analysis to be $s = 0.9674$. Regression coefficients R^2 and R^2 (adj) are found to be 98.59 and 97.39 respectively which indicates that model can explain the variation in size of ruthenium nanoparticles to the extent of 98.59 % which makes the model adequate to represent the process.

The final ANOVA table for formation of ruthenium nanoparticles via microemulsion technique, showing the significant factor (main effects and interactions) and their percentage contribution, is shown in Table 5. The significant main effect terms and interaction terms in the ANOVA Table 5 are computed using the F ratio as a test statistic (2).

Pareto chart

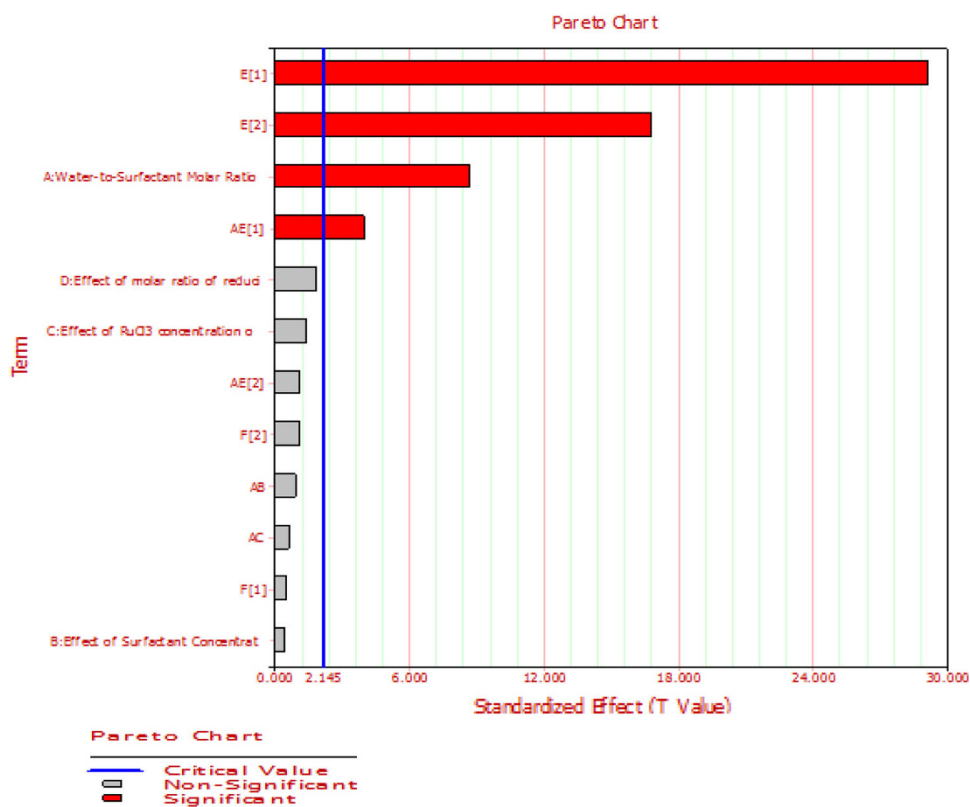
A PARETO chart is used to visually describe the significant and non-significant terms in synthesis of ruthenium nanoparticles by microemulsion method (Fig. 6).

Table 4 ANOVA Table

Source of variation	Degrees of freedom	Sum of squares (sequential)	Mean squares (sequential)	<i>F</i> ratio	<i>P</i> value
<i>A</i> water-to-surfactant molar ratio	1	71.6006	71.6006	76.5091	4.77E–07
<i>B</i> effect of surfactant concentration	1	0.0249	0.0249	0.0266	0.8727
<i>C</i> effect of RuCl ₃ concentration	1	1.1603	1.1603	1.2398	0.2843
<i>D</i> effect of molar ratio of reducing agent	1	6.6576	6.6576	7.114	0.0184
<i>E</i> effect of type of co-surfactant	2	805.7456	402.8728	430.4913	2.68E–13
<i>F</i> different reducing agent	2	16.0046	8.0023	8.5509	0.0037
<i>A</i> × <i>B</i>	1	0.5833	0.5833	0.6233	0.443
<i>A</i> × <i>C</i>	1	0.4975	0.4975	0.5316	0.478
<i>A</i> × <i>E</i>	2	16.2621	8.1311	8.6885	0.0035
Residual (error)	14	13.1018	0.9358		
Total	26	931.6383			

Table 5 Final ANOVA table showing only significant factors

Source of variation	Degrees of freedom	Sum of squares (sequential)	Mean squares (sequential)	<i>F</i> ratio	<i>P</i> value	Percentage contribution (%)
<i>A</i> water-to-surfactant molar ratio	1	71.6006	71.6006	39.5375	4.77E–07	7.6855
<i>E</i> effect of type of co-surfactant	2	805.7456	402.8728	222.4588	2.68E–13	86.487
<i>A</i> × <i>E</i>	2	16.2621	8.1311	4.4898	0.0035	1.7455
Residual (pooled error)	21	38.0300	1.8110			4.082
Total	26	931.6383				

Fig. 6 PARETO chart for Ru nanoparticles by microemulsion method

A PARETO chart is used to determine the importance of an effect. The standardized PARETO chart shown contains a bar for each effect, sorted from most significant to least significant. The length of each bar is proportional to the standardized effect, which is equal to the magnitude of the statistic that would be used to test the statistical significance of that effect. A vertical line is drawn at the location of the 0.05 critical values for Student's. Any bars that extend to the right of that line indicate effects that are statistically significant at the 5 % significance level.

In the present study, from PARETO chart it is seen that the effect of different co-surfactants and water-to-surfactant molar ratio are the significant factors. In addition, interaction between the above two factors is significant.

Conclusion

This study had shown the application of Taguchi OA Factorial Design method to identify the performance evaluation of microemulsion technique for synthesis of ruthenium nanoparticles. Authors tried to find out optimum parameters to synthesize the smallest ruthenium nanoparticles with narrow size distribution by this method. By using orthogonal experimental design and analysis technique, the system performance was analyzed in better way through only a small number of simulation experiments. ANOVA was carried out to identify the significant factors affecting particle size as well as size distribution and the best possible factor level combination was determined through.

Open Access This article is distributed under the terms of the Creative Commons Attribution License which permits any use, distribution, and reproduction in any medium, provided the original author(s) and the source are credited.

References

- Charinpanitkul T, Chanagul A, Dutta J, Rungsardthong U, Tanthapanichakoon W (2005) Effects of cosurfactant on ZnS nanoparticles synthesis in microemulsion. *Sci Technol Adv Mater* 6:266–271
- Clements RB (1991) Handbook of statistical methods in manufacturing. Prentice Hall, Englewood Cliffs, NJ
- Debouttiere P-J, Martinez V, Philippot K, Chaudret B (2009) An organometallic approach for the synthesis of water-soluble ruthenium and platinum nanoparticles. *Dalton Trans* 38(46):10172–10174
- He Y, Vinodgopal K, Muthupandian A, Grieser F (2006) Sonochemical synthesis of ruthenium nanoparticles. *Res Chem Intermed* 32:709–715
- Kim T, Kobayashi K, Nagai M (2007) Preparation and characterization of platinum–ruthenium bimetallic nanoparticles using reverse microemulsions for fuel cell catalyst. *J Oleo Sci* 56(10):553–562
- Lazic ZR (2004) Design of experiments in chemical engineering. Wiley, New Jersey
- Lopez-Quintela MA, Tojo C, Blanco MC, Garcia Rio L, Leis JR (2004) Microemulsion dynamics and reactions in microemulsion. *Curr Opin Colloid Interface Sci* 9:264–278
- Lu F, Liu J, Xu J (2008) Synthesis of chain-like Ru nanoparticle arrays and its catalytic activity for hydrogenation of phenol in aqueous media. *Mater Chem Phys* 108:369–374
- Mendenhall W, Sincich T (1989) Statistics for the engineering and computer sciences, 2nd edn. Maxwell Macmillan International Editions, San Francisco
- Motoyama Y, Takasaki M, Higashi K, Yoon SH, Mochida I, Nagashima H (2006) Highly-dispersed and size-controlled ruthenium nanoparticles on carbon nanofibers: preparation, characterization, and catalysis. *Chem Lett* 35:876–877
- Nandanwar SU, Chakraborty M, Mukhopadhyay S, Shenoy KT (2011a) Stability of ruthenium nanoparticles synthesized by solvothermal method. *Cryst Res Technol* 46:393–399
- Nandanwar SU, Chakraborty M, Murthy ZVP (2011b) Formation of ruthenium nanoparticles by the mixing of two reactive microemulsions. *Ind Eng Chem Res* 50:11445–11451
- Patharkar RG, Nandanwar SU, Chakraborty M (2013) Synthesis of colloidal ruthenium nanocatalyst by chemical reduction method. *J Chem* 2013:1–5
- Rojas S, Garcia-Garcia FJ, Jaras S, Martinez-Huerta MV, Garcia Fierro JL, Boutonnet M (2005) Preparation of carbon supported Pt and PtRu nanoparticles from microemulsion electrocatalysts for fuel cell applications. *Appl Catal A* 285(1–2):24–35
- Xiong L, Manthiram A (2005) Catalytic activity of Pt–Ru alloys synthesized by a microemulsion method in direct methanol fuel cells. *Solid State Ion* 176:385–392
- Yan X, Liu H, Liew KY (2001) Size control of polymer-stabilized ruthenium nanoparticles by polyol reduction. *J Mater Chem* 11:3387–3391
- Zawadzki M, Okal J (2008) Synthesis and structure characterization of Ru nanoparticles stabilized by PVP or γ -Al₂O₃. *Mater Res Bull* 43:3111–3121
- Zhang X, Zhang F, Guan RF, Chan KY (2007a) Preparation of Pt–Ru–Ni ternary nanoparticles by microemulsion and electrocatalytic activity for methanol oxidation. *Mater Res Bull* 42(2):327–333
- Zhang Y, Yu J, Niu H, Liu H (2007b) Synthesis of PVP-stabilized ruthenium colloids with low boiling point alcohols. *J Colloid Interface Sci* 313:503–510